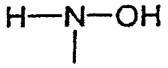
Claims

1. A method for producing organosilicon compounds having carbonyl radicals by oxidation of organosilicon compounds having carbinol radicals with the aid of a mediator selected from the group consisting of the aliphatic, cycloaliphatic, heterocyclic and aromatic NO-, NOH- and

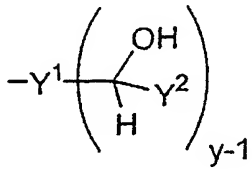


-containing compounds and of an oxidizing agent.

2. The method as claimed in claim 1, characterized in that the organosilicon compounds having carbinol radicals which are used are those containing units of the formula

$$A'_aR_bX_cH_dSiO_{(4-a-b-c-d)/2} \quad (I),$$

in which A' may be identical or different and are a radical of the formula



(II)

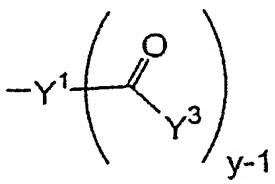
Y^1 is a divalent or polyvalent, linear or cyclic, branched or straight-chain organic radical which optionally may be substituted and/or interrupted by the atoms N, O, P, B, Si or S,
Y^2 is a hydrogen atom or a monovalent, linear or cyclic, branched or straight-chain, organic radical which optionally may be substituted and/or interrupted by the atoms N, O, P, B, Si or S,
y, depending on the valency of radical Y^1, is ≥ 2,
R may be identical or different and are a monovalent, linear or cyclic, branched or

straight-chain optionally substituted hydrocarbon radical,
X may be identical or different and are a chlorine atom, a radical of the formula $-OR^1$ where R^1 is a hydrogen atom or alkyl radical having 1 to 18 carbon atom(s), which may be substituted by ether oxygen atoms, a monovalent, linear or cyclic, branched or straight-chain hydrocarbon radical which optionally may be interrupted by units $-C(O)-$, $-C(O)O-$, $-C(O)NR^1-$, $-O-C(O)O-$, $-O-C(O)NR^1-$, $-NR^1-C(O)-NR^1-$, $-NR^1-$, $-(NR^1_2)^+-$, $-O-$, $-S-$ or $=N-$ and may be substituted by hydroxyl, mercapto, amino, ammonium, carbonyl, carboxyl or oxiranyl groups, or are the group A',
a is 0, 1 or 2,
b is 0, 1, 2 or 3,
c is 0, 1, 2 or 3, and
d is 0, 1, 2 or 3,
with the proviso that the sum a+b+c+d is ≤ 4 and the organosilicon compounds of the formula (I) have at least one radical A' per molecule.

3. The method as claimed in claim 1, characterized in that organosilicon compounds having carbonyl radicals which are obtained are those containing units of the formula

$$A_aR_bX_cH_dSiO_{(4-a-b-c-d)/2} \quad (III),$$

in which A may be identical or different and are a radical of the formula



(IV)

Y^3 is a hydrogen atom or a monovalent, linear or

cyclic, branched or straight-chain organic radical which optionally may be substituted and/or interrupted by the atoms N, O, P, B, Si or S, and Y^1, R, X, a, b, c, d and y have the meanings stated therefor in claim 2,
with the proviso that the sum a+b+c+d is ≤4 and the organosilicon compounds of the formula (III) have at least one radical A per molecule.

4. The method as claimed in claim 1 or 2, characterized in that organosilicon compounds having carbinol radicals which are used are those of the formula

$$A'_vR_wX_{(3-v-w)}Si \qquad (I'),$$

in which A', X and R have the meaning stated therefor in claim 2,
v is 0, 1, 2 or 3, preferably 0 or 1,
w is 0, 1, 2 or 3,
with the proviso that they contain at least one radical A' per molecule.

5. The method as claimed in claim 1 or 2, characterized in that organosilicon compounds having carbinol radicals which are used are those of the formula

$$A'_vR_{3-v}SiO(SiR_2O)_n(SiRA'O)_oSiR_{3-v}A'_v \qquad (I''),$$

in which A' and R have the meaning stated therefor in claim 2,
v is 0, 1, 2 or 3, preferably 0 or 1,
n is 0 or an integer from 1 to 2000,
o is 0 or an integer from 1 to 2000, preferably from 0 to 500,
with the proviso that they contain at least one radical A' per molecule.

6. The method as claimed in claim 1 or 2, characterized in that organosilicon compounds having carbinol radicals which are used are those of the formula

$$[A'_vR_{3-v}SiO_{1/2}]_s[SiO_{4/2}] \qquad (I'''),$$

in which A' and R have the meanings stated therefor in claim 2,
v is 0, 1, 2 or 3, preferably 0 or 1,
s may assume a value of from 0.2 to 6, preferably from 0.4 to 4, inclusive, and describes the number of M units $[A'_vR_{3-v}SiO_{1/2}]$ per Q unit $[SiO_{4/2}]$,
with the proviso that they contain at least one radical A' per molecule.

7. The method as claimed in claim 1 or 3, characterized in that organosilicon compounds having carbonyl radicals which are obtained are those of the formula

$$A_vR_wX_{(3-v-w)}Si \qquad (III'),$$

in which A, X and R have the meanings stated therefor in claim 3,
v is 0, 1, 2 or 3, preferably 0 or 1,
w is 0, 1, 2 or 3,
with the proviso that they contain at least one radical A per molecule.

8. The method as claimed in claim 1 or 3, characterized in that organosilicon compounds having carbonyl radicals which are obtained are those of the formula

$$A_vR_{3-v}SiO(SiR_2O)_n(SiRAO)_oSiR_{3-v}A_v \qquad (III''),$$

in which A and R have the meanings stated therefor in claim 3,

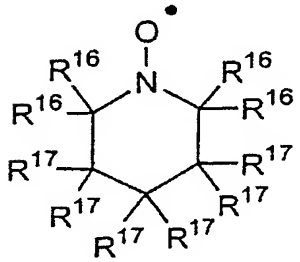
v is 0, 1, 2 or 3, preferably 0 or 1,
n is 0 or an integer from 1 to 2000,
o is 0 or an integer from 1 to 2000, preferably from 0 to 500,
with the proviso that they contain at least one radical A per molecule.

9. The method as claimed in claim 1 or 3, characterized in that organosilicon compounds having carbonyl radicals which are obtained are those of the formula

$$[A_vR_{3-v}SiO_{1/2}]_s[SiO_{4/2}] \qquad (III'''),$$

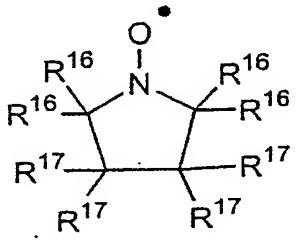
in which A and R have the meanings stated therefor in claim 3,
v is 0, 1, 2 or 3, preferably 0 or 1,
s may assume a value from 0.2 to 6, preferably from 0.4 to 4, inclusive, and describes the number of M units $[A_vR_{3-v}SiO_{1/2}]$ per Q unit $[SiO_{4/2}]$,
with the proviso that they contain at least one radical A per molecule.

10. The method as claimed in any of claims 1 to 9, characterized in that nitroxyl radicals of the formula



(XI)

or



(XII)

in which
R^{16} are identical or different and are a phenyl,

aryl-C_1-C_5-alkyl, C_1-C_{12}-alkyl, C_1-C_5-alkoxy, C_1-C_{10}-carbonyl and carbonyl-C_1-C_6-alkyl radical,
it being possible for the phenyl radicals to be unsubstituted or monosubstituted or polysubstituted by a radical R^{18} and for the aryl-C_1-C_5-alkyl, C_1-C_{12}-alkyl, C_1-C_5-alkoxy, C_1-C_{10}-carbonyl and carbonyl-C_1-C_6-alkyl radicals to be saturated or unsaturated, branched or straight-chain and to be monosubstituted or polysubstituted by a radical R^{18},
it being possible for R^{18} to be present once or several times and R^{18} being identical or different and being a hydroxyl, formyl or carboxyl radical, ester or salt of the carboxyl radical, carbamoyl, sulfono, sulfamoyl, nitro, nitroso, amino, phenyl, benzoyl, C_1-C_5-alkyl or C_1-C_5-alkoxy radical or a C_1-C_5-alkylcarbonyl radical,
R^{17} are identical or different and are a hydrogen atom or a hydroxyl, mercapto, formyl, cyano, carbamoyl or carboxyl radical, ester or salt of the carboxyl radical, sulfono radical, ester or salt of the sulfono radical, a sulfamoyl, nitro, nitroso, amino, phenyl, aryl-C_1-C_5-alkyl, C_1-C_{12}-alkyl, C_1-C_5-alkoxy, C_1-C_{10}-carbonyl and carbonyl-C_1-C_6-alkyl radical, phospho, phosphono or phosphonooxy radical, ester or salt of the phosphonooxy radical,
it being possible for the carbamoyl, sulfamoyl, amino, mercapto and phenyl radical to be unsubstituted or monosubstituted or polysubstituted by a radical R^{12},
and the aryl-C_1-C_5-alkyl, C_1-C_{12}-alkyl, C_1-C_5-alkoxy, C_1-C_{10}-carbonyl and carbonyl-C_1-C_6-alkyl radical may be saturated or unsaturated, straight-chain or branched and may be monosubstituted or polysubstituted by a radical R^{12}, and a [$-CR^{17}R^{17}-$] group may be replaced by oxygen, an optionally C_1-C_5-alkyl-substituted imino radical, a (hydroxy)imino radical, a carbonyl function or a

vinylidene function optionally monosubstituted or disubstituted by R^{12},
and two neighboring groups $[-CR^{17}R^{17}-]$ may be replaced by a group $[-CR^{17}=CR^{17}-]$, $[-CR^{17}=N-]$ or $[-CR^{17}=N(O)-]$,
it being possible for R^{12} to be present once or several times and R^{12} being identical or different and being a hydroxyl, formyl, cyano or carboxyl radical, ester or salt of the carboxyl radical, carbamoyl, sulfono, sulfamoyl, nitro, nitroso, amino, phenyl, C_1-C_5-alkyl, C_1-C_5-alkoxy or C_1-C_5-alkylcarbonyl radical,
are used as the mediator.

11. The method as claimed in claim 10, characterized in that the nitroxyl radicals of the formulae (XI) and (XII) are linked to a polymeric structure via one or more radicals R^{17}.

12. The method as claimed in claim 10 or 11, characterized in that mediators used are those selected from the group consisting of
2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO),
4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl,
4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl,
4-acetoxy-2,2,6,6-tetramethylpiperidin-1-oxyl,
4-benzoyloxy-2,2,6,6-tetramethylpiperidin-1-oxyl
and
PIPO (polymer immobilized piperidinyloxyl).

13. The method as claimed in any of claims 1 to 12, characterized in that the mediator is used in amounts of from 0.01 to 100 mol%, based on the amount of carbinol groups present in the organosilicon compound used.

14. The method as claimed in any of claims 1 to 13, characterized in that oxidizing agents used are those selected from the group consisting of air,

oxygen, hydrogen peroxide, organic peroxides, perborates and persulfates, organic and inorganic peracids, salts and derivatives of the peracids, chlorine, bromine, iodine, hypohalic acids and the salts thereof, for example in the form of bleaching liquor, halic acids and the salts thereof, halogen acids and the salts thereof, $Fe(CN)_6^{3-}$ and N-chloro compounds,
it being possible for them optionally to be used in each case in combination with enzymes.

15. The method as claimed in any of claims 1 to 14, characterized in that the oxidizing agent is a 2-electron oxidizing agent and is used in amounts of from 0.1 to 125 mol%, based on the amount of carbinol groups present in the organosilicon compounds used.

16. The method as claimed in any of claims 1 to 13, characterized in that oxidizing agents used are metal oxides or anodes of electrolysis cells.

17. The method as claimed in any of claims 1 to 16, characterized in that it is carried out continuously.

18. The use of the organosilicon compounds having carbonyl radicals and prepared by the methods 1 to 17 for the treatment of surfaces.

19. The use of the organosilicon compounds having carbonyl radicals and prepared by the methods 1 to 17 in cosmetic formulations.

20. The use of the organosilicon compounds having carbonyl radicals and prepared by the methods 1 to 17 as surface-active agents.

21. The use of the organosilicon compounds having

carbonyl radicals and prepared by the methods 1 to 17 as a reactive intermediate for chemical syntheses.

22. The use of the organosilicon compounds having carbonyl radicals and prepared by the methods 1 to 17 as free radical transfer agents in free radical polymerization processes.